Thermodynamic Properties of Mixtures of Refrigerants R-32, R-125, R-134a, and R-152a¹

E.W. Lemmon^{2,3,4} and R.T Jacobsen²

¹ Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

² Center for Applied Thermodynamic Studies, University of Idaho, Moscow, ID 83844-1011

³ Current Address: Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80303

⁴ To whom correspondence should be addressed.

ABSTRACT

A mixture model explicit in Helmholtz energy has been developed which is capable of predicting thermodynamic properties of refrigerant mixtures containing R-32, R-125, R-134a, or R-152a. The Helmholtz energy of the mixture is the sum of the ideal gas contribution, the compressibility (or real gas) contribution, and the contribution from mixing. The contribution from mixing is given by a single equation which is applied to all mixtures used in this work. The independent variables are the reduced density and reduced temperature. The model may be used to calculate thermodynamic properties of mixtures at various compositions including dew and bubble point properties and critical points. It incorporates the most accurate published equation of state for each pure fluid. The model may be used to calculate the properties of mixtures generally within the experimental accuracies of the available measured properties. The estimated accuracy of calculated properties is $\pm 0.1\%$ in density, $\pm 0.5\%$ in the speed of sound, and $\pm 1\%$ in heat capacities. Calculated bubble point pressures are generally accurate to within 1%.

KEY WORDS: equation of state; mixtures; R-32; R-125; R-134a; R-152a; thermodynamic properties.

1. INTRODUCTION

Applications requiring the use of equations of state capable of accurate prediction of thermodynamic properties of environmentally-safe refrigerant mixtures are increasing. New refrigerants and mixtures of refrigerants are used as environmentally acceptable replacements for chlorofluorocarbons and hydrochlorofluorocarbons in refrigeration, heat pumps, foam-blowing, and other applications. Mixture equations are required to evaluate the performance of possible alternatives to the fully halogenated chlorofluorocarbons as working fluids. Many of the refrigerant mixtures form azeotropes. This is often desirable in vapor compression cycles because the mixture behaves as a pure fluid during phase changes.

The model presented here for mixtures of refrigerants is part of a more generalized model reported by Lemmon and Jacobsen [1] for mixtures of cryogens, hydrocarbons, and refrigerants. This model was initially reported by Lemmon [2] in a slightly different format. The model is based on corresponding states theory. Reducing parameters which are dependent on the mole fraction are used to modify absolute values of density and temperature. The Helmholtz energy for an ideal solution is determined at the reduced density and temperature of the mixture using accurate pure fluid equations of state for the mixture components.

The portion of the model describing the Helmholtz energy contribution from mixing is nearly the same for all binary mixtures, and relatively simple scaling factors are used to determine its magnitude for a particular application. Experimental data from many different mixtures were used to determine the function. The model is capable of predicting mixture properties for fluids with limited experimental databases. In addition, all vapor and liquid thermodynamic properties, including density, energy, entropy, heat capacity, sound speed, vapor-liquid equilibrium, and the mixture critical temperature, pressure, and density, can be calculated accurately using this approach.

The mixtures studied in this work are:

- R-32/R-125
- R-32/R-134a

- R-125/R-134a
- R-32/R-125/R-134a
- R-134a/R-152a

Data for these mixtures were used to evaluate the behavior of the model, to calculate the coefficients of the generalized refrigerant mixture equation and to calculate the individual parameters for each binary mixture. Table I lists the pure fluid equations of state used in this work. All equations were converted for convenience from the published format to a fundamental form widely used in system analysis and design.

2. THE MIXTURE EQUATION FOR ENVIRONMENTALLY-SAFE REFRIGERANTS

The Helmholtz energy for mixtures of refrigerants can be calculated using

$$\alpha_m(\delta, \tau, \mathbf{x}) = \alpha_m^i(\delta, \tau, \mathbf{x}) + \alpha^E(\delta, \tau, \mathbf{x}). \tag{1}$$

The Helmholtz energy for the ideal solution is

$$\alpha_m^i(\delta, \tau, \mathbf{x}) = \sum_{i=1}^r x_i \left[\alpha_i^0(\delta, \tau) + \alpha_i^r(\delta, \tau) + \ln x_i \right], \tag{2}$$

where r is the number of fluids in the mixture, α_i^0 is the ideal gas Helmholtz energy of component i, and α_i^r is the residual Helmholtz energy of component i. Equations for the ideal gas Helmholtz energy and residual Helmholtz energy for the pure fluids are given in the references shown in Table I.

The contribution to the Helmholtz energy from mixing used in this work is

$$\alpha^{E} = \sum_{p=1}^{r} \sum_{q=p+1}^{r} x_{p} x_{q} F_{pq} \sum_{k=1}^{10} N_{k} \delta^{i_{k}} \tau^{j_{k}} + x_{R-32} x_{R-125} (N_{11} \delta \tau + N_{12} \delta) + x_{R-32} x_{R-134a} N_{13} \delta, \quad (3)$$

where the N_k , i_k , and j_k are coefficients and exponents obtained from linear regression of experimental mixture data. The coefficients, N_k , of the equation are determined using a stepwise least-squares technique with a search and selection procedure which selects an optimum group of terms from a large comprehensive function based on statistical evaluation of the significance of individual terms. All thermodynamic properties can be calculated from

the Helmholtz energy using differentiation with respect to density or temperature as described by Lemmon *et al.* [3].

The independent parameters of the equation for the contribution to the Helmholtz energy from mixing given in this work are reduced density and temperature and mixture composition. In addition, one other parameter, F_{pq} , is required which relates the excess-like properties of one binary mixture to those of another. This value is determined with a nonlinear fitting procedure that minimizes the sum of squares of the deviations between the equation and the data for a small select set of measurements.

The reduced density and temperature of the mixture are

$$\delta = \rho / \rho_i \text{ and} \tag{4}$$

$$\tau = T_i / T \quad , \tag{5}$$

where T_i and ρ_i are the reducing values,

$$T_{j} = \sum_{p=1}^{r} x_{p} T_{c_{p}} + \sum_{p=1}^{r} \sum_{q=p+1}^{r} x_{p} x_{q} \zeta_{pq}$$

$$\tag{6}$$

$$\rho_{j} = \left[\sum_{p=1}^{r} \frac{x_{p}}{\rho_{c_{p}}} + \sum_{p=1}^{r} \sum_{q=p+1}^{r} x_{p} x_{q} \xi_{pq} \right]^{-1}, \tag{7}$$

and where ζ_{pq} and ξ_{pq} are used to define the shapes of the reducing parameter lines. The units for temperature and density are kelvins and mol·dm⁻³. These reducing parameters are not the same as the critical parameters of the mixture and the use of these parameters allows the calculation of VLE properties above the reducing temperature. These parameters define the relationship between the critical lines of different binary mixtures and are determined simultaneously in the nonlinear fit with the generalized factor. Details of the fitting procedures to determine the generalized factors and mixture parameters are given by Lemmon [2] and are not repeated here. The values of the coefficients and exponents in Eq. (3) are given in Table II. The generalized factors and mixture parameters are given in Table III.

3. COMPARISONS OF CALCULATED REFRIGERANT MIXTURE PROPERTIES TO EXPERIMENTAL DATA

Summary comparisons of values calculated using the mixture equation to P- ρ -T data, isochoric heat capacity data, sound speed data and VLE data for refrigerant mixtures are given in Table IV, as well as the temperature and composition range for the first component listed. Details of the property calculation methods including those for VLE states are given by Lemmon [2].

The accuracies of calculated values of various properties are determined by comparing them to measured values. Statistical analyses are used to determine the overall estimated accuracy of the model in representing the data sets used in determining the coefficients of equations of state, and to define the ranges of estimated accuracies for various properties calculated with the formulation.

The statistics used to evaluate the equation are based on the percent deviation for any property, X,

$$\% \Delta X = 100 \left(\frac{X_{\text{data}} - X_{\text{calc}}}{X_{\text{data}}} \right). \tag{8}$$

Using this definition, the statistics in Table IV are defined as:

$$AAD = \frac{1}{n} \sum_{i=1}^{n} \left| \% \Delta X_i \right| \tag{9}$$

$$Bias = \frac{1}{n} \sum_{i=1}^{n} \left(\% \Delta X_i \right) \tag{10}$$

Two of the terms listed in Eq. (3) are specific to the R-32/R-125 binary mixture and another is specific to the R-32/R-134a binary mixture. The mixture model behavior is sensitive to the accuracy of the pure fluid equations of state. The equation of Outcalt and McLinden [5] for R-32 was used in place of the equation from Tillner-Roth and Yokozeki [4] to determine the sensitivity of the deviations of calculated properties to the selection of the R-32 equation. Replacing the equation increased the AAD for the data of Magee [11] by 20%. The deviations for other data in the supercritical region increased as well. The

database for mixtures containing R-32 may be more reliable than that for the pure fluid. Additional details of this analysis are given by Lemmon [2]. This issue may be resolved by additional measurements and a revised correlation for R-32. Likewise, there are similar deficiencies in the R-125 database in the critical region.

4. ACCURACY ASSESSMENT

An assessment has been made to determine the accuracy of the mixture model reported here. Generally, the equation is accurate to $\pm 0.1\%$ in density, $\pm 1\%$ in heat capacity, and $\pm 0.5\%$ for the speed of sound. For binary mixtures, calculated bubble point pressures are generally within $\pm 1\%$. The model is valid between from 200 to 450 K up to 60 MPa as verified by experimental data. In regions where there are no binary mixture data, the accuracy is estimated to be of the same magnitude. However, this cannot be verified by the authors until experimental data are available to support these conclusions. Although the equation was developed using mostly binary data, it is accurate in calculating the properties of mixtures with three or more constituents. This conclusion is based upon comparisons of calculated values to the limited data available for multicomponent systems.

Future measurements will confirm whether the equation is valid for other mixtures and in regions not covered by the experimental data used in the development of this model. These data will enable continued evaluation and development of the model.

REFERENCES

- 1. E.W. Lemmon and R.T Jacobsen, submitted to *Int. J. Thermophys.* (1997).
- E.W. Lemmon, <u>A Generalized Model for the Prediction of the Thermodynamic</u>
 <u>Properties of Mixtures Including Vapor-Liquid Equilibrium</u>, Ph.D. Dissertation,
 University of Idaho (1996).
- 3. E.W. Lemmon, R.T Jacobsen, S.G. Penoncello, and S.W. Beyerlein, *Adv. Cryo. Eng.* 39:1891 (1994).
- 4. R. Tillner-Roth and A. Yokozeki, to be submitted to *J. Phys. Chem. Ref. Data* (1997).
- 5. S.L. Outcalt and M.O. McLinden, *Int. J. Thermophys.* <u>16</u>(1):79 (1995).
- 6. R. Tillner-Roth and H.D. Baehr, *J. Phys. Chem. Ref. Data* 23(5):657 (1994).

- 7. R. Tillner-Roth, *Int. J. Thermophys.* <u>16</u>(1):91 (1995).
- 8. C.D. Holcomb, VLE data reported in: Haynes, W.M, <u>Thermophysical Properties of HCFC Alternatives</u>, National Institute of Standards and Technology, Boulder, Colorado, Final Report for ARTI MCLR Project Number 660-50800 (1996).
- 9. H. Kiyoura, J. Takebe, H. Uchida, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* 41:1409 (1996).
- M. Kleemiss, <u>Thermodynamic Properties of Binary and Ternary Mixtures of R134a</u>, <u>R32, R125 and R143a - Measurements and Equations of State</u>, Dissertation, University of Hannover, Germany (1996).
- 11. J.W. Magee, private communication, NIST, Boulder, Colorado, USA (1995).
- K. Oguchi, T. Takaishi, N. Yada, T. Namiki, and T. Sato, Kanagawa Institute of Technology, Japan (1995).
- 13. C.-C. Piao, I. Iwata, and M. Noguchi, to be submitted to *J. Chem. Eng. Data*, Mech. Eng. Lab., Daikin Industries, Ltd., Japan (1996).
- 14. T. Sato, H. Kiyoura, H. Sato, and K. Watanabe, Int. J. Thermophys. 17:43 (1996).
- 15. L.A. Weber and D.R. Defibaugh, *Int. J. Thermophys.* <u>15</u>(5):863 (1994).
- 16. H.-L. Zhang, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* 41:1401 (1996).
- 17. D.R. Defibaugh and G. Morrison, Int. J. Refrig. 18(8):518 (1995).
- 18. K. Fujiwara, H. Momota, M. Noguchi, *13th Japan Symp. Thermophys. Prop.* <u>A11.6</u>:61 (1992).
- 19. Y. Higashi, 19th International Congress of Refrigeration, Netherlands IVa:297 (1995).
- 20. M. Nagel and K. Bier, Int. J. Refrig. 18:534 (1995).
- 21. J.V. Widiatmo, H. Sato, and K. Watanabe, High Temp.-High Press. 25:677 (1993).
- 22. T. Sato, H. Kiyoura, H. Sato, and K. Watanabe, J. Chem. Eng. Data <u>39</u>(4):855 (1994).
- 23. J.V. Widiatmo, T. Fujimine, H. Sato, and K. Watanabe, to be submitted to *J. Chem. Eng. Data* (1997).
- 24. Y. Higashi, Int. J. Thermophys. 16(5):1175 (1995).
- 25. J.V. Widiatmo, H. Sato, and K. Watanabe, Fluid Phase Equilib. 99:199 (1994).

- 26. T. Hozumi, H. Sato, and K. Watanabe, 4th Asian Thermophysical Properties Conference, Japan, p. 307 (1995).
- 27. M. Higuchi and Y. Higashi, Proc. 16th Japan Symp. Thermophys. Prop., Hiroshima, p. 5 (1995).
- 28. Y. Higashi, private communication, Department of Mechanical Engineering, Iwaki Meisei University, Japan (1996).
- 29. M. Dressner and K. Bier, <u>Thermodynamic Measurements in Binary Systems of New Refrigerants</u>, Fortschr.-Ber. VDI <u>3</u>(332) (1993).
- 30. R. Tillner-Roth, *J. Chem. Thermodyn.* <u>25</u>:1419 (1993).
- 31. A.J. Grebenkov, Yu.G. Kotelevsky, V.V. Saplitza, O.V. Beljaeva, T.A. Zajatz, and B.D. Timofeev, Proc, CFC's: The Day After, IIR Comm. B1, B2, E1, E2; Padova, Italy (1994).
- 32. M. Kleiber, M., Fluid Phase Equilib., 92:149 (1994).

Table I. Pure Fluid Equations of State for Refrigerants Used in the Mixture Model.

Fluid	Author	Temperature Range (K)	Maximum Pressure (MPa)
R-32	Tillner-Roth and Yokozeki [4]	160 - 500	60
R-125	Outcalt and McLinden [5]	174 - 500	68
R-134a	Tillner-Roth and Baehr [6]	169.85 - 500	70
R-152a	Tillner-Roth [7]	154.65 - 435	30

Table II. Coefficients and Exponents of the Mixture Equation

k	N_k	i_k	\dot{J}_k
1	-0.245476271425×10 ⁻¹	1	2
2	-0.241206117483	1	4
3	-0.513801950309×10 ⁻²	1	-2
4	-0.239824834123×10 ⁻¹	2	1
5	0.259772344008	3	4
6	-0.172014123104	4	4
7	0.429490028551×10 ⁻¹	5	4
8	-0.202108593862×10 ⁻³	6	0
9	-0.382984234857×10 ⁻²	6	4
10	0.262992331354×10 ⁻⁵	8	-2
11	-0.198606229861×10 ⁻¹	1	1
12	0.143226453485	1	0
13	0.369107330061×10 ⁻¹	1	0

Table III. Parameters of the Mixture Equation

Binary Mixture	F_{pq}	ξ_{pq}	ζ_{pq}
R-32/R-125	-0.789585	-0.00530177	14.663390
R-32/R-134a	-0.314574	-0.00392017	5.737916
R-125/R-134a	0.104729	0.0	-2.736948
R-134a/R-152a	0.125997	0.00487924	-2.041245

Table IV. Comparisons of Mixture Properties Calculated from the Model to Refrigerant Mixture Data

Author	No. Points	Temp. Range	Comp. Range	AAD	Bias	
R-32/R-125 <i>P</i> -ρ- <i>T</i>						
Holcomb [8]	45	279-341	0.24-0.96	0.940	0.361	
Kiyoura et al. [9]	94	330-440	0.37-0.61	0.487	-0.486	
Kleemiss [10]	415	243-413	0.50-0.51	0.187	-0.035	
Magee [11]	228	200-400	0.50	0.145	0.039	
Oguchi et al. [12]	6	355-430	0.87	0.275	-0.138	
Piao <i>et al</i> . [13]	533	263-393	0.37-0.90	0.245	-0.098	
Sato <i>et al.</i> [14]	156	320-440	0.70-0.90	0.333	-0.328	
Weber and Defibaugh [15]	17	338-373	0.55	0.497	-0.497	
Zhang et al. [16]	124	300-380	0.50-0.70	0.279	-0.273	
Overall	1618	200-440	0.24-0.96	0.263	-0.112	
R-32/R-125 VLE						
Defibaugh and Morrison [17]	10	249-338	0.76	0.151	-0.060	
Fujiwara et al. [18]	8	273	0.06-0.90	2.060	2.060	
Higashi [19]	45	283-346	0.23-0.90	0.329	0.322	
Holcomb [8]	30	280-340	0.34-0.95	0.311	0.172	
Kleemiss [10]	23	224-333	0.48-0.52	0.364	-0.227	
Nagel and Bier [20]	34	205-345	0.24-0.95	0.504	0.019	
Oguchi et al. [12]	11	250-350	0.87	0.432	0.432	
Piao <i>et al</i> . [13]	10	263-283	$0.37 \text{-} 0.90^*$	0.665	-0.648	
Widiatmo et al. [21]	24	280-310	0.20-0.90	0.530	0.383	
Overall	195	205-350	0.06-0.95	0.476	0.192	

Table IV. (Continued)

Author	No. Points	Temp. Range	Comp. Range	AAD	Bias
R-32/R-134a <i>P</i> -ρ- <i>T</i>					
Holcomb [8]	44	279-340	0.13-0.97	1.123	0.535
Kleemiss [10]	390	243-413	0.50-0.56	0.090	0.001
Magee [11]	219	200-400	0.50	0.121	-0.079
Oguchi et al. [12]	19	363-473	0.39	0.426	0.407
Piao et al. [13]	633	263-393	0.33-0.89	0.405	-0.225
Sato <i>et al</i> . [22]	220	320-440	0.33-0.89	0.147	-0.011
Weber and Defibaugh [15]	17	338-373	0.51	1.048	-1.048
Widiatmo et al. [23]	22	280-330	0.40	0.105	-0.003
Overall	1564	200-473	0.13-0.97	0.274	-0.095
R-32/R-134a c _v					
Magee [11]	131	205-343	0.50	0.373	0.294
R-32/R-134a w					
Hozumi et al. [26]	144	303-343	0.16-0.90	0.030	0.030
R-32/R-134a VLE					
Defibaugh and Morrison [17]	25	253-358	0.50-0.55	0.398	0.260
Fujiwara et al. [18]	6	273-273	0.20-0.92	3.262	-3.262
Higashi [24]	39	283-365	0.12-0.67	1.171	1.104
Holcomb [8]	48	280-340	0.16-0.78	0.400	0.127
Kleemiss [10]	16	223-343	0.42-0.52	0.229	0.118
Nagel and Bier [20]	50	203-369	0.21-0.77	0.480	0.136
Oguchi et al. [12]	34	238-301	0.27-0.71	0.868	0.776
Piao et al. [13]	10	261-283	$0.33 \text{-} 0.89^*$	0.565	-0.565
Widiatmo et al. [25]	30	280-340	0.33-0.89	1.646	1.646
Overall	258	203-369	0.12-0.92	0.801	0.445

Table IV. (Continued)

Author	No. Points	Temp. Range	Comp. Range	AAD	Bias
R-125/R-134a <i>P</i> -ρ- <i>T</i>					
Holcomb [8]	17	280-342	0.35-0.72	0.297	-0.166
Kleemiss [10]	407	243-413	0.50-0.51	0.125	-0.103
Magee [11]	268	200-400	0.50	0.110	-0.076
Weber and Defibaugh [15]	18	303-373	0.50	0.378	-0.353
Widiatmo et al. [23]	110	280-350	0.09-0.92	0.112	-0.093
Overall	820	200-413	0.09-0.92	0.128	-0.100
R-125/R-134a VLE					
Higuchi and Higashi [27]	55	283-365	0.18-0.78	0.373	0.030
Holcomb [8]	40	280-340	0.26-0.65	0.521	-0.032
Kleemiss [10]	24	224-343	0.46-0.51	0.432	-0.326
Nagel and Bier [20]	31	206-365	0.25-0.75	0.541	0.219
Widiatmo et al. [23]	75	280-350	0.09-0.92	0.712	0.711
Overall	225	206-365	0.09-0.92	0.542	0.235
R-32/R-125/R-134a P-ρ-T					
Holcomb [8]	42	244-346	0.20-0.68	0.984	0.490
Kiyoura et al. [9]	105	315-440	0.38-0.52	0.481	0.254
Kleemiss [10]	369	243-413	0.33-0.35	0.093	-0.019
Oguchi et al. [12]	12	365-430	0.38-0.47	0.090	-0.023
Piao et al. [13]	994	263-393	0.19-0.47	0.307	-0.115
Widiatmo et al. [23]	53	280-340	0.38-0.46	0.185	-0.181
Overall	1575	243-440	0.19-0.68	0.278	-0.056

Table IV. (Continued)

Author	No. Points	Temp. Range	Comp. Range	AAD	Bias
R-32/R-125/R-134a VLE					
Higashi [28]	52	273-359	0.17-0.54	0.624	-0.235
Holcomb [8]	58	221-345	0.05-0.60	0.901	0.030
Kleemiss [10]	44	222-353	0.14-0.66	0.372	-0.306
Nagel and Bier [20]	29	205-362	0.19-0.43	0.601	-0.160
Piao et al. [13]	31	270-326	0.32-0.38	0.664	0.165
Widiatmo et al. [23]	43	280-340	0.35-0.46	0.504	0.500
Overall	257	205-362	0.05-0.66	0.625	-0.007
R-134a/R-152a P-ρ-T					
Dressner and Bier [29]	139	333-423	0.49-0.54	0.225	-0.076
Tillner-Roth [30]	1679	243-433	0.25-0.75	0.073	0.034
Weber and Defibaugh [15]	11	353-373	0.50	0.042	0.017
Overall	1829	243-433	0.25-0.75	0.085	0.025
R-134a/R-152a w					
Grebenkov et al. [31]	120	230-336	0.69	0.466	-0.446
R-134a/R-152a VLE					
Defibaugh and Morrison [17]	13	248-368	0.78	0.284	0.009
Kleiber [32]	25	255-298	0.31-0.98	0.146	-0.134
Tillner-Roth [30]	65	243-378	0.23-0.75	0.071	-0.035
Overall *Down point compositions	103	243-378	0.12-0.98	0.116	-0.054

^{*}Dew point compositions